

UC Irvine

UC Irvine Previously Published Works

Title

Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities.

Permalink

<https://escholarship.org/uc/item/12j8v7nb>

Journal

Environmental science & technology, 48(18)

ISSN

0013-936X

Authors

Xue, Likun
Wang, Tao
Louie, Peter KK
[et al.](#)

Publication Date

2014-09-01

DOI

10.1021/es503278g

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Increasing External Effects Negate Local Efforts to Control Ozone Air Pollution: A Case Study of Hong Kong and Implications for Other Chinese Cities

Likun Xue,^{*,†,‡} Tao Wang,^{*,†,‡} Peter K. K. Louie,[‡] Connie W. Y. Luk,[‡] Donald R. Blake,[§] and Zheng Xu[†]

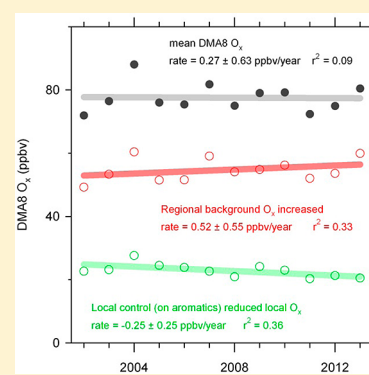
[†]Department of Civil and Environmental Engineering, the Hong Kong Polytechnic University, Hong Kong, China

[‡]Environmental Protection Department, the Government of Hong Kong Special Administrative Region, Hong Kong, China

[§]Department of Chemistry, University of California at Irvine, Irvine, California, United States

Supporting Information

ABSTRACT: It is challenging to reduce ground-level ozone (O_3) pollution at a given locale, due in part to the contributions of both local and distant sources. We present direct evidence that the increasing regional effects have negated local control efforts for O_3 pollution in Hong Kong over the past decade, by analyzing the daily maximum 8 h average O_3 and O_x ($=O_3+NO_2$) concentrations observed during the high O_3 season (September–November) at Air Quality Monitoring Stations. The locally produced O_x showed a statistically significant decreasing trend over 2002–2013 in Hong Kong. Analysis by an observation-based model confirms this decline in in situ O_x production, which is attributable to a reduction in aromatic hydrocarbons. However, the regional background O_x transported into Hong Kong has increased more significantly during the same period, reflecting contributions from southern/eastern China. The combined result is a rise in O_3 and a nondecrease in O_x . This study highlights the urgent need for close cross-boundary cooperation to mitigate the O_3 problem in Hong Kong. China's air pollution control policy applies primarily to its large cities, with little attention to developing areas elsewhere. The experience of Hong Kong suggests that this control policy does not effectively address secondary pollution, and that a coordinated multiregional program is required.



1. INTRODUCTION

Ozone (O_3) is a principal component of photochemical smog, a form of air pollution that is rife within urban-industrialized regions. High concentrations of O_3 can adversely affect the health of humans, crops, and vegetation, and may alter the climate.^{1–3} The ambient O_3 at a given location is produced by a variety of precursors, namely nitrogen oxides ($NO_x=NO+NO_2$), carbon monoxide (CO) and volatile organic compounds (VOCs), which may be emitted either locally or from distances even hundreds of kilometres away.^{4,5} Therefore, a major challenge of O_3 pollution regulation is to deal with processes and contributions on different scales.

Ozone pollution has posed an ongoing challenge to researchers and policy makers since it was first discovered in Los Angeles in the 1950s.⁶ Recent compilations of long-term monitoring data indicate success in the implementation of pollution-control measures in some metropolitan areas in North America, for example, Los Angeles (California's South Coast Air Basin),⁷ New York (the Northeastern U.S. urban corridor)⁸ and Houston.^{8,9} NO_x and VOCs have been significantly reduced in both these cities and the surrounding areas.^{8,10,11} In contrast, the air quality in China has deteriorated over the last three decades, due to the nation's rapid urban-industrialization. This deterioration includes emergence of widespread ground-level O_3 pollution.^{12–14} Hong Kong is

situated on the South China coast, adjacent to the rapidly developing Pearl River Delta (PRD) region (Supporting Information (SI) Figure S1). As Hong Kong has far outstripped mainland China in terms of economic development and environmental regulation (note that Hong Kong and mainland China constitute one country with two administrative systems) and is downwind of mainland China in autumn/winter monsoon seasons, it provides a unique opportunity to evaluate the effectiveness of local efforts to control O_3 pollution against the backdrop of an ongoing increase in O_3 -precursor emissions in the surrounding regions.

Like virtually all other metropolitan areas, Hong Kong has for many years suffered from serious air-pollution problems, including early reports of photochemical smog in the mid-1990s.¹⁵ To improve the territory's air quality, the Hong Kong government has since implemented long-term and step-by-step measures to reduce the emissions of NO_x , CO and VOCs from vehicles, power plants, industrial, commercial and residential activities (see http://www.epd.gov.hk/epd/english/environmentinhk/air/prob_solutions/strategies_apc.html for

Received: July 6, 2014

Revised: August 8, 2014

Accepted: August 18, 2014

Published: August 18, 2014

details of the air pollution control program). As a result, the anthropogenic emissions of O_3 precursors have significantly decreased since the 1990s (see SI Figure S2 for the estimated emission inventory data). However, this reduction in local emissions does not appear to have alleviated the O_3 pollution problem in Hong Kong. Previous studies have shown that the O_3 concentration in both the background and urban atmospheres increased at an average rate of 0.58 ppbv/year during 1994–2007,¹⁶ and suggested considerable contributions from regional transport in the PRD and super-regional transport from eastern China.^{16–18} Thus, it is crucial to quantify the contributions of local and external sources to O_3 trends in Hong Kong and to assess the effectiveness of local pollution-reduction measures.

In this study, we used data obtained from the Air Quality Monitoring Network by the Hong Kong Environmental Protection Department (HKEPD) to analyze the O_3 trends over 2002–2013 as well as the local and regional contributions. An observation-based box model (OBM) was then used with the most comprehensive data at a polluted site (Tung Chung) to verify trends in local O_3 production and to evaluate the effects of reducing individual O_3 precursors. The results of the analysis provide solid evidence that the government's control efforts have reduced local ozone production in Hong Kong. However, due to increasing contributions from southern/eastern China, the overall O_3 concentration has risen. We discuss the implications of Hong Kong's experience for other Chinese cities.

2. MATERIALS AND METHODS

2.1. Data Source. We analyzed the air-quality data (i.e., O_3 , CO and NO_x) collected at 11 Air Quality Monitoring Stations (AQMS; see SI Figure S1) in Hong Kong during the autumn season (September–November) of 2002–2013. The autumn data was chosen because it is the period when Hong Kong suffers from severe photochemical O_3 pollution and is generally located downwind of mainland China under Asian monsoons.^{16,19} The instrumentation, quality assurance and control protocols implemented by the Hong Kong AQMS are similar to those used in the US's air-quality monitoring program. Continuous measurements were available at most AQMS over 2002–2013, with occasional data gaps at 1 or 2 sites in several years (see Table S1 for an overview of the data availability at each AQMS). The daily maximum 8-h average (DMA8) O_3 concentrations, upon which the ambient air quality standards in Hong Kong (75 ppbv) are based, were subject to the analysis. To take into consideration the titration of O_3 by fresh NO emissions, O_x was used instead of O_3 to determine the regional and local contributions.

The data obtained at Tung Chung (see also SI Figure S1) were subject to a more-detailed OBM analysis, for the following reasons: (1) this site is located in the area of Hong Kong that experiences the most serious O_3 pollution;²⁰ and (2) the measurements taken at this site comprised the most comprehensive source of data, including long-term observations of hydrocarbons and short-term intensive measurements of oxygenated VOCs (OVOCs) and nitrous acid (HONO). We have two sets of hydrocarbon measurements. One was made by using canister sampling coupled with laboratory detection by gas chromatography (GC) with flame-ionization detection (FID), electron-capture detection and mass-spectrometry detection, which is an internationally recognized system for VOC measurements and has been utilized in dozens of

previous studies (the chemical analysis of samples was carried out at the University of California at Irvine).^{21,22} The other set comprised the real-time measurements obtained by a combination of GC separation, photoionization detection and FID detection (Syntech Spectras, model GC955 Series 600/800 POCP; it consists of two systems for detection of C_2 – C_5 and C_6 – C_{10} hydrocarbons respectively). The canister data covered a wide range of nonmethane hydrocarbon (NMHC) species (C_2 – C_{10} ; >50 species) at a relatively low time resolution (normally one 24 h sample per week). In comparison, the real-time data had a high time resolution (30 min) but only covered ~30 major C_2 – C_9 NMHC species. Canister measurements were available for 2002, 2006, 2007, and 2011, and the validated real-time data covered the period of 2008–2012. Overall, both measurements showed good agreement for alkanes and aromatics but large discrepancy for alkenes (see SI Figure S3 for an intercomparison). It is still not clear about the reason for the discrepancy in ambient alkenes measurements (note that our periodical intercomparison by sampling the same standards showed good agreement between both methods). Considering that the real-time instrument sometimes may not work well for alkenes (especially the low-carbon species) and that the canister measurements are usually believed to be more reliable, we corrected the real-time data according to the canister data in the base analysis. Besides, we conducted another set of analysis with canister data corrected by real-time data, and found that our major conclusions remained unchanged (see SI for a detailed evaluation).

2.2. Determination of Regional Background and Locally Produced Ozone. We utilized the method proposed by the Texas Commission on Environmental Quality (TCEQ)^{9,23,24} to determine the “regional background O_x ” transported into the Hong Kong area. Ten AQMS (except for Sham Shui Po site; see SI Figure S1) were selected based on their locations near the urban perimeter and distances from local emission sources. These sites are believed to be capable of measuring regional background O_x when any of them is upwind of the Hong Kong urban area. The regional background O_x can be estimated as the lowest DMA8 O_x concentration recorded by these sites. We also computed the area-wide peak O_x as the highest DMA8 O_x value observed at all of the AQMS (including Sham Shui Po). The locally produced O_x can be determined as the difference between the peak O_x and regional background O_x . The regional background and locally produced O_x were estimated every day for the autumn seasons of 2002–2013.

Berlin et al. recently evaluated the uncertainties of the TCEQ determination of regional background ozone,⁹ which may be overestimated with recirculation of aged local plumes with O_3 produced in the preceding days, and be underestimated if there was a large spatial gradient in background O_x . Such uncertainties are inevitable for all the observation-based studies. Here it should be recognized that our derived “local O_x ” refers to the O_x produced photochemically in Hong Kong within 1 day. Another uncertainty relates to the weak sea breeze penetrating partially and affecting only a few coastal sites, which may also lead to underestimation of background O_x . This problem should be small in the present study given the dominance of continental outflow from mainland China in autumn. A somewhat subjective but stringent method was adopted here to reduce this problem. We examined the time series obtained at all AQMS, and chose the days on which the DMA8 O_x at the coastal site (i.e., Tap Mun) was distinctly

lower than those at all the other sites and DMA8 O_3 at Hok Tsui. For such days, the lowest DMA8 O_x at the noncoastal sites was regarded as the regional background O_x . Only 23 days (2.1%) out of 1092 were revised, and the regional background O_x was increased on average by 17.8 ppbv on these days. Despite the high data capture rates (normally >97%) at AQMS, some data gaps remain (e.g., at KT in 2002; see SI Table S1), which may also raise uncertainty in the regional background O_x determination. It is difficult to accurately quantify such uncertainty, but it should be small in view of the facts that the TCEQ method uses the data at ten AQMS (using only the maximum and minimum O_x) and that the KT data were generally moderate among all AQMS.

We compared the regional background O_x determined by the TCEQ method with the DMA8 O_3 observed at Hok Tsui, a remote background station of Hong Kong (see the results in SI Figure S4).¹⁶ NO_2 was not routinely measured at Hok Tsui, but its concentrations are generally very low at midday compared to O_3 according to our previous observations.²⁵ Overall, the TCEQ background O_x exhibited a good agreement with the O_3 at Hok Tsui, with a slope of 1.01 ± 0.03 (95% confidence intervals) and r^2 of 0.74. This suggests that the TCEQ method provides a reasonable measure of the regional background O_x entered Hong Kong.

2.3. Observation-Based Model. An observation-based chemical box model was used to estimate in situ O_3 production and its sensitivity to changes in O_3 precursors. In brief, the model was based on the Master Chemical Mechanism (MCM v3.2), an explicit mechanism describing the degradation of 143 primary VOCs together with the latest IUPAC inorganic nomenclature.^{26–28} In addition to chemistry, we considered physical processes such as dry deposition and atmospheric dilution with evolution of the planetary boundary layer. The photolysis frequencies appropriate for Hong Kong were parametrized using a two-stream isotropic-scattering model under clear-sky conditions (we did not consider the impact on O_3 production of the variation in solar radiations, and the rationale of this study is just to evaluate the effect of O_3 precursor changes), and were calculated within the model as a function of the solar zenith angle.^{28,29} A detailed description of this model, which we have used in previous studies,^{12,30} is given in the SI.

We performed model calculations for the years of 2002 and 2006–2012, during which the VOC measurements were available. The model was constrained by the autumn-average diurnal profiles of O_3 , CO , SO_2 , NO , NO_2 , CH_4 , C_2 – C_{10} NMHCs, H_2O , temperature and pressure measured at Tung Chung. To facilitate a more reasonable modeling analysis, we also prescribed the model with the measurements of OVOCs (17 species; see SI), HONO and aerosol surface density collected at Tung Chung during an intensive campaign in the autumn of 2011 (assuming constant levels for all years). We also conducted sensitivity analysis without constraints of the measured HONO. The results indicated that our major conclusions were unchanged (see SI for a full discussion).

The model read the measurement data every hour to calculate in situ O_x production, destruction and net rates. The model was run with 00:00 local time (LT) as the initial time. For each simulation, the model preran for 9 days to ensure that it approached a steady state necessary to stabilize the concentrations of unconstrained species. The output of the 10th day was then subject to further analyses. We also

estimated the sensitivity of O_3 production to changes in various O_3 precursors by conducting sensitivity model runs.

3. RESULTS

3.1. O_3/O_x Trends. Figure 1a shows the trends of the autumn-average DMA8 O_3 and O_x observed in Hong Kong

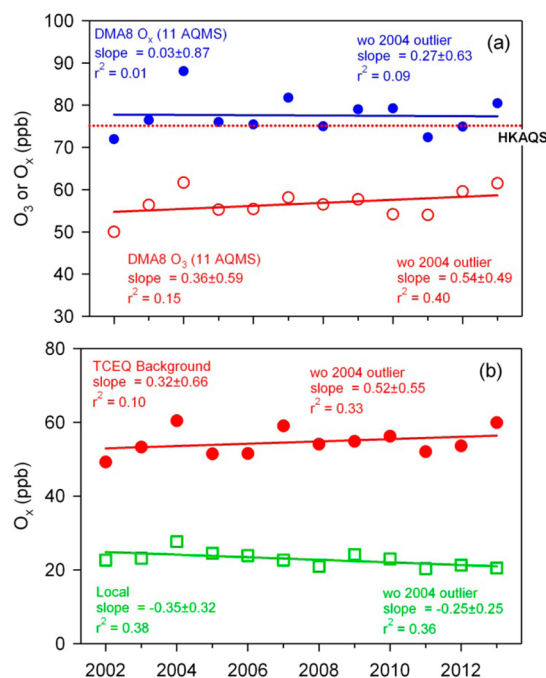


Figure 1. (a) Trends in autumn mean (September–November) DMA8 O_3 and O_x ($O_3 + NO_2$) recorded by 11 AQMS stations. The HKAQS O_3 concentration (75 ppbv) is indicated by the red dotted line. (b) Trends in regional background and local O_x estimated by the TCEQ method. Linear regressions were made for all years (solid lines) and without the exceptional year 2004 (not shown), with slopes ($\pm 95\%$ confidence intervals) and R squares annotated.

between 2002 and 2013. A slightly increasing trend was found for O_3 with a change rate of 0.36 ± 0.59 ($\pm 95\%$ confidence intervals) ppbv/year, but this increase was of little statistical significance ($p = 0.21$). The poor statistics were mainly driven by the outlying measurements in 2004. If the 2004 data was excluded from the regression, a clear and statistically significant upward trend ($p = 0.037$) with a larger amplitude (0.54 ± 0.49 ppbv/year) would be obtained. 2004 was an unusual year during which Hong Kong and the PRD region suffered from an extremely unfavorable weather condition.³¹ More intense sunlight and the dry weather facilitated stronger production of O_3 in the region.³¹ Hence in the subsequent discussion the O_3/O_x trends only refer to those derived from analysis of data without the 2004 outlier. In comparison with O_3 , O_x showed a smaller rise (0.27 ± 0.63 ppbv/year) but the trend was not statistically significant. Overall, these long-term observations indicate a rise in ambient O_3 and a nondecrease in O_x in Hong Kong over the past decade.

Figure 1b documents the average regional background O_x and locally produced O_x determined by the TCEQ method in the autumn of 2002–2013. The regional background O_x transported into Hong Kong composed on average approximately 70% of the DMA8 O_x concentrations, and explained 75% of the measured variability in DMA8 O_x (see SI Figure S5). In general, the locally produced O_x only contributed about

30% to the observed DMA8 O_x . To make these results in perspective, the average concentrations of both regional and local O_x on all days were estimated at 54 and 23 ppbv respectively, contributing to a total mean DMA8 O_x of 77 ppbv. For the O_3 nonattainment days (i.e., days with DMA8 O_3 exceeding 75 ppbv), in comparison, the mean regional and local O_x increased to 77 and 38 ppbv, sustaining a total average DMA8 O_x of 115 ppbv. These results indicate the dominant contribution of regional transport to the ambient O_x in Hong Kong.

Figure 1b also shows opposite trends in the regional background O_x and local O_x in Hong Kong. The regional background O_x have increased at 0.52 ± 0.55 ppbv/year in the past decade, though the trend was only of marginal statistical significance ($p = 0.06$). A single-tailed Student's t test suggests that the probability that the trend is positive is about 0.97. The increasing amplitude also agrees well with that determined for surface O_3 at Hok Tsui (a background site in Hong Kong; 0.58 ppbv/year) during the 1994–2007 period.¹⁶ On the contrary, the locally produced O_x showed a clear and statistically significant downward trend ($p = 0.05$) but with a smaller rate (-0.25 ± 0.25 ppbv/year). The above analyses reveal clearly that the local O_x has been reduced but the transported regional O_x has increased more significantly, and their combined effect resulted in a rise in O_3 and a nondecrease in O_x in Hong Kong.

3.2. Trends in O_3 Precursors. It is of interest to find the cause of reduction in the locally produced O_x in Hong Kong. For this purpose, we examined the trends of major O_3 precursors obtained at AQMS. Figure 2a clearly displays the statistically significant decreasing trends in the mean concentrations of CO, NO_x , and NO_2 observed at all available AQMS (i.e., 9 for NO_x , 11 for NO_2 and 4 for CO) in the autumn months between 2002 and 2013: CO showed a mean rate of

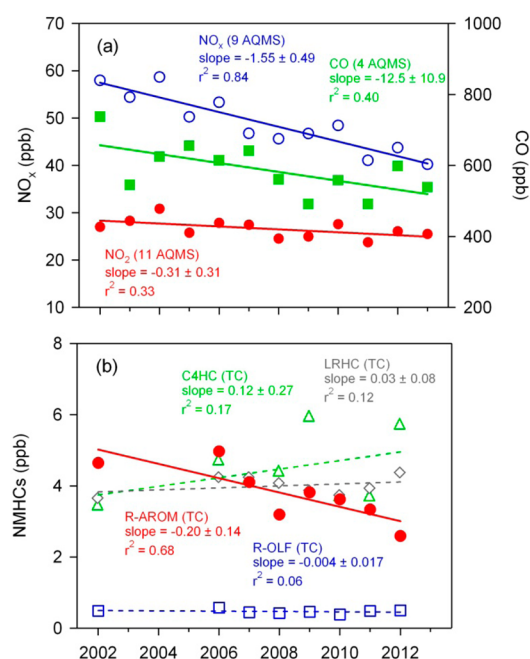


Figure 2. (a) Trends in autumn mean (September–November) NO_x , NO_2 , and CO observed at all available AQMS in Hong Kong. (b) Trends for major anthropogenic hydrocarbons measured at Tung Chung (the most polluted AQMS). The fit lines indicate linear regressions with slopes ($\pm 95\%$ confidence intervals) and R squares annotated.

change of -12.5 ± 10.9 ppbv/year; NO_x and NO_2 decreased by 1.55 ± 0.49 and 0.31 ± 0.31 ppbv/year, respectively. The trends at individual AQMS were also downward and statistically significant, despite the large variance in change rates at different sites (see SI Figure S6 and S7). The decrease in ambient concentrations of CO and NO_x is unsurprising, considering the persistent and step-by-step efforts made by the Hong Kong government in the last few decades to control and cut emissions from transportation, power plants and other industrial activities (see SI Figure S2 for reduction in the estimated emissions).

In Hong Kong, photochemical O_3 production is generally more sensitive to VOCs.²⁰ Figure 2b presents the average concentrations of major NMHCs measured at Tung Chung (the only AQMS with long-term VOC observations) in the autumn months of 2002–2012. To facilitate analysis and interpretation, the anthropogenic NMHC species were categorized into four groups, namely, reactive aromatics (R-AROM; including all aromatics except for benzene), reactive olefins (R-OLF, including all alkenes other than ethene; note that the ethene data obtained from the real-time GC measurements were not reliable and that ethene only presents a minor contributor to O_3 production in Hong Kong.²⁰ Thus, ethene was not considered in this analysis), alkanes with ≥ 4 carbons (C4HC) and hydrocarbons with low reactivity (LRHC; including ethane, propane and benzene). The ambient levels of reactive aromatics clearly declined over the period of study ($p = 0.012$), with a mean change rate of -0.20 ± 0.14 ppbv/year. This is an expected result of the strict VOC-control measures undertaken by the Hong Kong government. In April 2007, for instance, Hong Kong implemented the VOC Regulation, which was designed to control the VOC content (mainly aromatics) of architectural paints/coatings, printing inks, and six broad categories of consumer products. This Regulation was amended in October 2009 to extend control to additional products with high aromatic-VOC content. In comparison, despite the various control measures implemented by the government, we observed no significant trends in the concentrations of other NMHC groups (i.e., R-OLF, C4HC, and LRHC). The use of liquefied petroleum gas, which was not under effective control in Hong Kong until 2013, may be responsible for the sustained levels of certain VOC species (e.g., alkenes and butanes). Overall, these observations confirm that the ambient levels of CO, NO_x , and aromatic VOCs in Hong Kong have decreased in response to local control efforts. In the next section, we further evaluate their contributions to the reduced local O_3 production by the OBM analysis.

3.3. Changes in Local Ozone Production. Figure 3 presents the trends in the OBM-calculated daytime-average (09:00–18:00 LT) net O_x production rates at Tung Chung for the years of 2002 and 2006–2012, during which the VOC measurements were available. Consistent with the observed decline in the locally produced O_x concentrations, the in situ net O_x production rate showed a clear and statistically significant downward trend (-0.26 ± 0.25 ppbv/h/year, $p = 0.04$; see the red solid circles). This finding confirms the reduction in local ozone production in Hong Kong.

To evaluate the impact of the O_3 precursor changes on local O_3 production, a number of sensitivity model runs were conducted for the 2006–2012 period, with 2002 as a baseline. The base models for 2006–2012 were rerun with most of their parameters unchanged but with constraints to target O_3 precursors based on the 2002 data (i.e., assuming no change

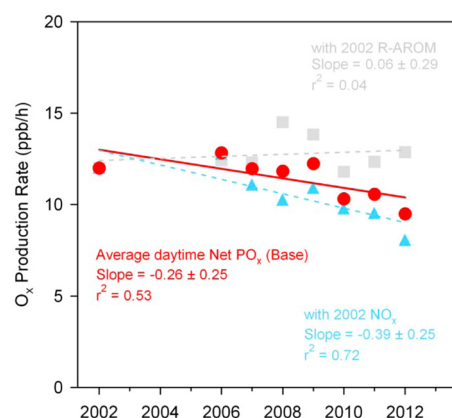


Figure 3. Trends in daytime-average net O_3 production rate calculated by the OBM at Tung Chung. The red circles indicate the true trends from the base models, and the gray squares and sky-blue triangles show the “trends” if the reactive aromatics or NO_x unchanged with respect to the year 2002. The fit lines denote linear regression with slopes ($\pm 95\%$ confidence intervals) and R squares annotated.

in each target precursor since 2002). The differences in the net O_3 production rates between the sensitivity and base runs can thus be ascribed to the changes in target precursors. The results are also presented in Figure 3. It is clear that if the levels of reactive aromatics had remained the same from 2002 onward, the net O_3 production rates between 2006 and 2012 would have been significantly higher than those determined from the base runs (see gray squares), and the trend of decreasing in situ O_3 production would have been broken. For example, if the levels of R-AROM had not decreased between 2002 and 2012 (despite decreasing levels of the other species), the net O_3 production rate in 2012 would have been ~ 12.9 ppbv/h, which is much higher than the result given by the base model (~ 9.5 ppbv/h), and comparable to the 2002 result (~ 12.0 ppbv/h). This indicates that the reduction of R-AROM should be the key factor leading to decreasing local O_3 production in Hong Kong. In contrast, if the NO_x concentration had remained at the level observed in 2002, the net O_3 production rates between 2006 and 2012 would have been even lower than the base results (see blue triangles), and a more significant decrease in local O_3 production would have been established at Tung Chung. In comparison, variations in ambient CO, R-OLF, C4HC, and LRHC levels had little effect on local O_3 production, as indicated by the comparability of the sensitivity and base model results for O_3 production rate when these precursors were examined (figure not shown).

It is also critical to the future O_3 pollution control to determine whether the chemical regime of local O_3 production has altered in response to the changing levels of ozone precursors. We calculated by the OBM the relative incremental reactivity (RIR) of major O_3 precursors at Tung Chung in 2002, 2007, and 2012, to identify the changes in local O_3 production regime over the past decade. RIR is defined as the ratio of decrease in O_3 production rate to decrease in precursor concentrations, and can be used to estimate the effects of a given emission reduction on ambient O_3 concentrations.³² The OBM-calculated RIRs for the major O_3 precursors are shown in Figure 4. Two aspects of the figure are of interest. First, there was no qualitative change in the O_3 production regime derived at Tung Chung between 2002 and 2012. O_3 production was found to be VOC-limited, particularly sensitive to reactive aromatics, and NO_x generally had a negative influence on

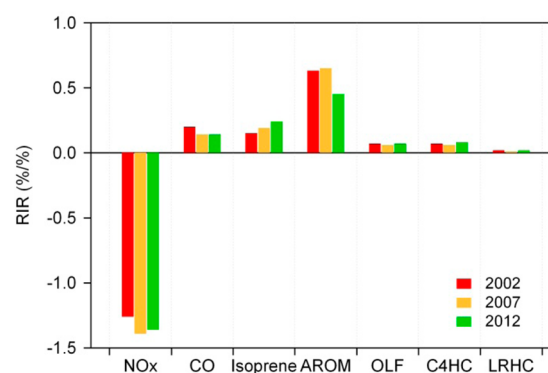


Figure 4. OBM-calculated RIRs for major O_3 precursors at Tung Chung in 2002, 2007, and 2012.

attempts to control O_3 production (due to the titration effect). These characteristics are consistent with those determined at five sites (including Tung Chung) in Hong Kong in 2002.²⁰ Second, the RIR of R-AROM showed a considerable quantitative decrease between 2007 (RIR = 0.65) and 2012 (RIR = 0.45). This is attributable to the reduction in reactive aromatics in Hong Kong (see Figure 2b). Based on the analysis, it is concluded that further reducing the levels of reactive aromatics is currently still the most effective way of minimizing local O_3 production in Hong Kong.

4. DISCUSSION AND IMPLICATIONS

As evidenced by the present study, although the control measures implemented by the Hong Kong government have effectively mitigated local O_3 formation, these efforts have been negated by the increase of regional influences. The rise in regional background O_3 levels is believed to be due to the increase in O_3 levels in the PRD region, along with the contributions of “super-regional” transport from the upwind regions beyond the PRD, that is, eastern China. Over the last few decades, the anthropogenic emissions of NO_x and VOCs have sharply increased across eastern China due to economic expansion and increasing energy use.^{33–35} Indeed, it has been confirmed that the atmospheric O_3 levels in several of the most urbanised regions of eastern China, namely the North China Plain, the Yangtze River Delta and the PRD, have shown an upward trend in the past decade.^{13,16,36–38} This increase in “background” O_3 , due mainly to regional (PRD-originating) and super-regional (eastern China based) contributions, has offset the reduction of local ozone production in Hong Kong, leading to an overall increase in ambient O_3 levels. However, without local control efforts would have definitely resulted in a more significant increase in ambient O_3 levels in Hong Kong. To successfully control its ozone problem in the future, therefore, Hong Kong must collaborate closely with mainland China, not only the PRD but also the entirety of eastern China.

This study also has important implications for efforts to reduce secondary pollution in other Chinese cities. The findings of recent studies have indicated that ozone pollution is becoming more extensive and more severe in the major urban-industrialized regions of China,^{12,14,39} and the ozone problem will be undoubtedly among China’s key environmental management targets in the near future. In the past, China’s air-pollution control has been limited to a few megacities (Beijing, Shanghai, and Guangzhou), partly due to more imminent needs to clean its air for hosting the 29th Summer Olympics, the 40th

World Expo., and the 16th Asian Games, respectively. Although these measures have helped to lessen primary pollution, they do not seem to have been sufficient in reducing ozone and other secondary pollutants.^{40,41} Even the unprecedentedly stringent pollution-control measures implemented in the Beijing Municipality before the Olympics in summer of 2008 did not significantly reduce ozone and sulfate aerosol pollution, due to the strong influence of regional pollution sources south of Beijing.⁴¹ The long-term data analyzed in the present study in Hong Kong vividly illustrate the importance of dealing with pollution sources over a large geographical area. As many other cities in central and eastern China are closer to regional sources of pollution, it is vital to develop and implement coordinated multiregional policies to mitigate ozone pollution and other secondary problems in these cities.

■ ASSOCIATED CONTENT

■ Supporting Information

Table S1; Figures S1–S7; description of the measured hydrocarbon and OVOC species; description of the observation-based box model; results of sensitivity modeling analysis with real-time alkenes measurements; impact of the HONO treatment on the OBM analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*(T.W.) Phone: (852) 2766-6059; fax: (852) 2334-6389; e-mail: cetwang@polyu.edu.hk.

*(L.X.) Phone: (852) 2766-6059; fax: (852) 2334-6389; e-mail: xuelikun@gmail.com.

Present Address

[†]Department of Civil and Environmental Engineering, the Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the HKEPD for providing the air-quality data, and the University of Leeds for providing the Master Chemical Mechanism (v3.2). We thank the referee who assessed our previous manuscript and gave very helpful suggestions for improving our study. This study was funded by the Hong Kong Environment and Conservation Fund (project no. 7/2009), the HKEPD (tender ref 06911-01136) and the Hong Kong Polytechnic University (1-ZV9N). The opinions expressed in this paper are those of the authors and do not necessarily reflect the views or policies of the Government of the Hong Kong Special Administrative Region, nor does mention of trade names or commercial products constitute an endorsement or recommendation of their use.

■ REFERENCES

- (1) *Rethinking the Ozone Problem in Urban and Regional Air Pollution*; National Research Council: Washington, D.C., 1991.
- (2) Chameides, W. L.; Li, X. S.; Tang, X. Y.; Zhou, X. J.; Luo, C.; Kiang, C. S.; St John, J.; Saylor, R. D.; Liu, S. C.; Lam, K. S.; Wang, T.; Giorgi, F. Is ozone pollution affecting crop yields in China? *Geophys. Res. Lett.* **1999**, *26* (7), 867–870.
- (3) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Inter-*

governmental Panel on Climate Change; Intergovernmental Panel on Climate Change: Cambridge, UK, 2007.

(4) Hidy, G. M. Ozone process insights from field experiments Part I: Overview. *Atmos. Environ.* **2000**, *34* (12–14), 2001–2022.

(5) Sillman, S. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmos. Environ.* **1999**, *33* (12), 1821–1845.

(6) Haagen-Smit, A. J. Chemistry and physiology of Los Angeles Smog. *Ind. Eng. Chem.* **1952**, *44* (6), 1342–1346.

(7) Pollack, I. B.; Ryerson, T. B.; Trainer, M.; Neuman, J. A.; Roberts, J. M.; Parrish, D. D. Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: A synthesis of measurements from 1960 to 2010. *J. Geophys. Res., Atmos.* **2013**, *118* (11), 5893–5911.

(8) Parrish, D. D.; Singh, H. B.; Molina, L.; Madronich, S. Air quality progress in North American megacities: A review. *Atmos. Environ.* **2011**, *45* (39), 7015–7025.

(9) Berlin, S. R.; Langford, A. O.; Estes, M.; Dong, M.; Parrish, D. D. Magnitude, decadal changes, and impact of regional background ozone transported into the greater Houston, Texas, Area. *Environ. Sci. Technol.* **2013**, *47*, 13985–13992.

(10) McDonald, B. C.; Dallmann, T. R.; Martin, E. W.; Harley, R. A., Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales. *J. Geophys. Res., Atmos.* **2012**, *117*.

(11) Warneke, C.; de Gouw, J. A.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Atlas, E.; Blake, D.; Trainer, M.; Parrish, D. D., Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions. *J. Geophys. Res., Atmos.* **2012**, *117*.

(12) Xue, L. K.; Wang, T.; Gao, J.; Ding, A. J.; Zhou, X. H.; Blake, D. R.; Wang, X. F.; Saunders, S. M.; Fan, S. J.; Zuo, H. C.; Zhang, Q. Z.; Wang, W. X. Ozone production in four major cities of China: Sensitivity to ozone precursors and heterogeneous processes. *Atmos. Chem. Phys. Discuss.* **2013**, *13*, 27243–27285.

(13) Shao, M.; Tang, X. Y.; Zhang, Y. H.; Li, W. J. City clusters in China: Air and surface water pollution. *Front. Ecol. Environ.* **2006**, *4* (7), 353–361.

(14) Wang, T.; Ding, A. J.; Gao, J.; Wu, W. S., Strong ozone production in urban plumes from Beijing, China. *Geophys. Res. Lett.* **2006**, *33*, (21).

(15) Wang, T.; Lam, K. S.; Lee, A. S. Y.; Pang, S. W.; Tsui, W. S. Meteorological and chemical characteristics of the photochemical ozone episodes observed at Cape D'Aguilar in Hong Kong. *J. Appl. Meteorol.* **1998**, *37* (10), 1167–1178.

(16) Wang, T.; Wei, X. L.; Ding, A. J.; Poon, C. N.; Lam, K. S.; Li, Y. S.; Chan, L. Y.; Anson, M. Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994–2007. *Atmos. Chem. Phys.* **2009**, *9* (16), 6217–6227.

(17) Li, Y.; Lau, A. K. H.; Fung, J. C. H.; Ma, H.; Tse, Y. Y. Systematic evaluation of ozone control policies using an Ozone Source Apportionment method. *Atmos. Environ.* **2013**, *76*, 136–146.

(18) Li, Y.; Lau, A. K. H.; Fung, J. C. H.; Zheng, J. Y.; Zhong, L. J.; Louie, P. K. K., Ozone source apportionment (OSAT) to differentiate local regional and super-regional source contributions in the Pearl River Delta region, China. *J. Geophys. Res., Atmos.* **2012**, *117*.

(19) Lam, K. S.; Wang, T. J.; Chan, L. Y.; Wang, T.; Harris, J. Flow patterns influencing the seasonal behavior of surface ozone and carbon monoxide at a coastal site near Hong Kong. *Atmos. Environ.* **2001**, *35* (18), 3121–3135.

(20) Zhang, J.; Wang, T.; Chameides, W. L.; Cardelino, C.; Kwok, J.; Blake, D. R.; Ding, A.; So, K. L. Ozone production and hydrocarbon reactivity in Hong Kong, Southern China. *Atmos. Chem. Phys.* **2007**, *7*, 557–573.

(21) Simpson, I. J.; Blake, N. J.; Barletta, B.; Diskin, G. S.; Fuelberg, H. E.; Gorham, K.; Huey, L. G.; Meinardi, S.; Rowland, F. S.; Vay, S. A.; Weinheimer, A. J.; Yang, M.; Blake, D. R. Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C₂–C₁₀ volatile organic compounds (VOCs), CO₂, CH₄, CO, NO,

NO₂, NO_y, O₃ and SO₂. *Atmos. Chem. Phys.* **2010**, *10* (23), 11931–11954.

(22) Xue, L. K.; Wang, T.; Simpson, I. J.; Ding, A. J.; Gao, J.; Blake, D. R.; Wang, X. Z.; Wang, W. X.; Lei, H. C.; Jing, D. Z. Vertical distributions of non-methane hydrocarbons and halocarbons in the lower troposphere over northeast China. *Atmos. Environ.* **2011**, *45* (36), 6501–6509.

(23) Langford, A. O.; Senff, C. J.; Banta, R. M.; Hardesty, R. M.; Alvarez, R. J.; Sandberg, S. P.; Darby, L. S., Regional and local background ozone in Houston during Texas Air Quality Study 2006. *J. Geophys. Res., Atmos.* **2009**, *114*.

(24) Nielsen-Gammon, J., Tobin, J., McNeel, A., Li, G. A *conceptual model for eight-hour exceedences in Houston, Texas Part I: background ozone levels in Eastern Texas*; Houston, TX, 2005.

(25) Wang, T.; Lam, K. S.; Chan, L. Y.; Lee, A. S. Y.; Carroll, M. A. Trace gas measurements in coastal Hong Kong during the PEM-West B. *J. Geophys. Res., Atmos.* **1997**, *102* (D23), 28575–28588.

(26) Jenkin, M. E.; Saunders, S. M.; Derwent, R. G.; Pilling, M. J. Construction and application of a master chemical mechanism (MCM) for modelling tropospheric chemistry. *Abstr. Pap. Am. Chem. Soc.* **1997**, *214*, 116–COLL.

(27) Jenkin, M. E.; Saunders, S. M.; Wagner, V.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. *Atmos. Chem. Phys.* **2003**, *3*, 181–193.

(28) Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* **2003**, *3*, 161–180.

(29) Hayman, G. D. *Effects of Pollution Control on UV Exposure*, AEA Technology Final Report prepared for the Department of Health and Contract 121/6377; AEA Technology: Oxfordshire, UK, 1997.

(30) Xue, L. K.; Wang, T.; Guo, H.; Blake, D. R.; Tang, J.; Zhang, X. C.; Saunders, S. M.; Wang, W. X. Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: Results from the Mt. Waliguan Observatory. *Atmos. Chem. Phys.* **2013**, *13* (17), 8551–8567.

(31) Hong Kong Environmental Protection Department. *Air Quality in Hong Kong 2004: A Report on the Results from the Air Quality Monitoring Network*; Hong Kong, China, 2005.

(32) Cardelino, C. A.; Chameides, W. L. An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. *J. Air Waste Manage.* **1995**, *45* (3), 161–180.

(33) Lu, Q.; Zheng, J. Y.; Ye, S. Q.; Shen, X. L.; Yuan, Z. B.; Yin, S. S. Emission trends and source characteristics of SO₂, NO_x, PM₁₀, and VOCs in the Pearl River Delta region from 2000 to 2009. *Atmos. Environ.* **2013**, *76*, 11–20.

(34) Ohara, T.; Akimoto, H.; Kurokawa, J.; Horii, N.; Yamaji, K.; Yan, X.; Hayasaka, T. An Asian emission inventory of anthropogenic emission sources for the period 1980–2020. *Atmos. Chem. Phys.* **2007**, *7* (16), 4419–4444.

(35) Zhang, Q.; Streets, D. G.; Carmichael, G. R.; He, K. B.; Huo, H.; Kannari, A.; Klimont, Z.; Park, I. S.; Reddy, S.; Fu, J. S.; Chen, D.; Duan, L.; Lei, Y.; Wang, L. T.; Yao, Z. L. Asian emissions in 2006 for the NASA INTEX-B mission. *Atmos. Chem. Phys.* **2009**, *9* (14), 5131–5153.

(36) Ding, A. J.; Wang, T.; Thouret, V.; Cammas, J. P.; Nedelec, P. Tropospheric ozone climatology over Beijing: Analysis of aircraft data from the MOZAIC program. *Atmos. Chem. Phys.* **2008**, *8* (1), 1–13.

(37) Xu, X.; Lin, W.; Wang, T.; Yan, P.; Tang, J.; Meng, Z.; Wang, Y. Long-term trend of surface ozone at a regional background station in eastern China 1991–2006: Enhanced variability. *Atmos. Chem. Phys.* **2008**, *8* (10), 2595–2607.

(38) Zhang, Q.; Yuan, B.; Shao, M.; Wang, X.; Lu, S.; Lu, K.; Wang, M.; Chen, L.; Chang, C.-C.; Liu, S. C. Variations of ground-level O₃ and its precursors in Beijing in summertime between 2005 and 2011. *Atmos. Chem. Phys.* **2014**, *14*, 6089–6101.

(39) Zhao, C.; Wang, Y. H.; Zeng, T. East China Plains: A “basin” of ozone pollution. *Environ. Sci. Technol.* **2009**, *43* (6), 1911–1915.

(40) Liu, H.; Wang, X. M.; Zhang, J. P.; He, K. B.; Wu, Y.; Xu, J. Y. Emission controls and changes in air quality in Guangzhou during the Asian Games. *Atmos. Environ.* **2013**, *76*, 81–93.

(41) Wang, T.; Nie, W.; Gao, J.; Xue, L. K.; Gao, X. M.; Wang, X. F.; Qiu, J.; Poon, C. N.; Meinardi, S.; Blake, D.; Wang, S. L.; Ding, A. J.; Chai, F. H.; Zhang, Q. Z.; Wang, W. X. Air quality during the 2008 Beijing Olympics: Secondary pollutants and regional impact. *Atmos. Chem. Phys.* **2010**, *10* (16), 7603–7615.